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PHOTODISSOCIATION DYE LASER

Abraham Kasdan

Exxon Research and Engineering Company

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PHOTODISSOCIATION DYE LASER

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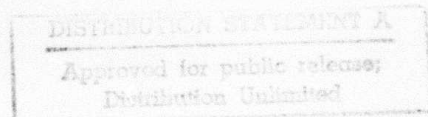
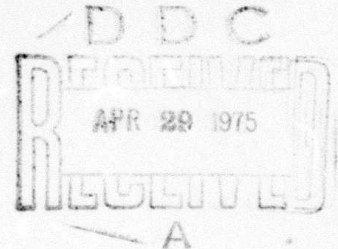
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The photodissociation dye laser is expected to exhibit several significant advantages over conventional dye lasers. Since the electronic structure of the radical is not characterized by singlet and triplet levels, the problems associated with intersystem transitions in conventional dyes are eliminated. In addition, the upper laser level lifetime of the radicals being studied as possible active media is expected to be at least an order of magnitude longer than that of conventional dyes, hence leading to the possibility of higher output powers. Continuous wave operation in such a laser scheme may be possible if the depletion rate of the lower laser level via radical recombination is sufficient to maintain the required population inversion.

The PDL program is now in its initial proof of principle phase. A number of promising chemical candidates for the active medium have been identified. The main thrust of the present effort is being directed towards obtaining data on the rates of those processes that are relevant to assessing the possibility of laser action in these systems. During the first six months of the PDL program, a number of accomplishments have been achieved:

A. Five promising PDL molecules have been synthesized and their absorption spectra characterized.

B. A pulsed tunable UV source has been assembled to investigate their fluorescence characteristics.

C. Hexaphenylethane has been identified as the most promising PDL candidate for an initial study.

D. Triphenylmethyl radical fluorescence has been observed in the hexaphenylethane system. The fluorescence lifetime has been measured and a number of experiments have been outlined that will measure parameters important to achieving laser action.

SUMMARY

The photodissociation dye laser (PDL) program is an effort to develop a new class of tunable liquid lasers operating in the visible region of the spectrum. In the PDL scheme, laser action occurs between an excited electronic state and the ground electronic state of radicals produced by the photodissociation of specific classes of molecules in solution.

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I. INTRODUCTION

The photodissociation dye laser (PDL) program is an effort to develop a new class of tunable liquid lasers operating in the visible region of the spectrum. In the PDL scheme, laser action occurs between an excited electronic state and the ground electronic state of radicals produced in the photodissociation of specific classes of molecules in solution. In this study, a class of highly strained ethanes, the hexaarylethanes is being investigated as potential laser media. Continuous wave operation of such lasers is expected based on the depletion of the radical ground state (the lower laser level) by the recombination to the original parent ethane structure. As in conventional dye laser systems, wavelength tunability is assured because the numerous vibrational and rotational modes of the complex molecule result in a quasi-continuous manifold of energy levels associated with each electronic level.

The photodissociation dye laser is expected to exhibit several significant advantages over conventional dye lasers. The radical can be thought of, to a first approximation, as a one-electron system. As a result, the electronic structure of the radical consists of doublet levels rather than the singlet and triplet level structure characteristic of the paired electrons of conventional dye molecules. Consequently, problems associated with non-radiative intersystem-crossing transitions which result in deleterious absorption by the lowest triplet level at the laser wavelength in conventional dye molecules are eliminated.

The second advantage of the PDL scheme is related to the upper laser level lifetime. In conventional laser dyes, the spontaneous radiative lifetime of the first excited singlet level is typically on the order of a few nanoseconds. In radical systems, however, there is evidence, both theoretical and experimental, that the first doublet-doublet electronic transitions are in some cases, partially forbidden. From the point of view of the PDL scheme, this means that the radiative lifetime of the upper laser level is one to two orders of magnitude longer than that exhibited by the upper laser level of conventional organic dyes. Consequently, a larger population density of the upper level may be obtained, thereby allowing the possibility of generating higher laser output power levels than can be presently attained with conventional dyes. In addition, the longer radiative lifetime favors the recombination of the radical ground state to the parent dimer at a sufficiently fast rate to permit a continuous population inversion and hence, cw laser action.

The PDL program is now in its initial proof of principle phase. A number of promising chemical candidates for the active medium have been identified. The main thrust of the present effort is being directed towards obtaining data on the rates of those processes that are relevant to assessing the possibility of laser action in these systems. During the first six months of the PDL program, a number of accomplishments have been achieved:

A. Five promising PDL molecules have been synthesized and their absorption spectra characterized.

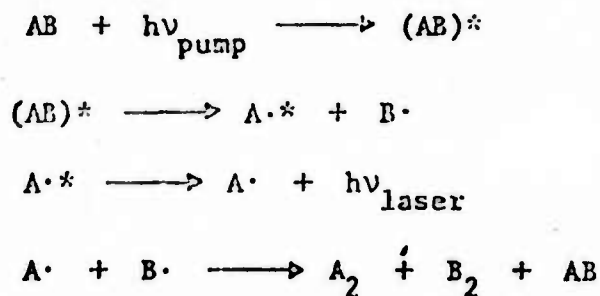
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D. Triphenylmethyl radical fluorescence has been observed in the hexaphenylethane system. The fluorescence lifetime has been measured and a number of experiments have been outlined that will measure parameters important to achieving laser action.

II. THE PHOTODISSOCIATION DYE LASER CONCEPT

In its most general form, the photodissociation dye laser may be understood as follows: A stable molecule, AB, in solution is optically pumped to its first excited singlet state. The absorbed pump energy exceeds the molecules dissociation energy and two radicals are formed upon dissociation. The excess energy is partitioned as electronic and vibrational excitation in one or both of the radicals A \cdot and B \cdot . In particular, we consider radical A \cdot to be electronically excited. A partial population inversion is produced between the first excited and the ground state of the radical. Laser action occurs in A \cdot and the resulting A \cdot and B \cdot ground state molecules are unstable against recombination. The processes may be written as:



In the final recombination step, not all of the radicals form the original molecule AB, but the dimeric forms A₂ and B₂ are also produced. Continuous laser action would require replenishment of the starting material, AB.

Let us consider in more detail the special case where B \equiv A so that the starting molecule is dimeric.

A. Molecular Structure and Kinetics

The general energy level scheme for such a photodissociation dye laser molecule is shown schematically in Figure 1. The stable parent dimer, having no unpaired electrons, exhibits the usual singlet and triplet level structure. The ground and excited electronic singlet levels are denoted by D_{S0}, D_{S1},...and the triplet levels are denoted by D_{T0}, D_{T1},...

The lowest electronic levels of the radicals, obtained from the symmetric photodissociation of the dimer, are shown adjacent to the dimer structure. The radical, having a single unpaired electron, exhibits a doublet structure. In the figure the radical ground state is shown displaced upward in energy from the dimer ground state by an amount equal to the dimer dissociation energy.

The vibrational level spacing in both the dimer and radical ranges between 150-1500 cm⁻¹ while the rotational spacing ranges between 15-150 cm⁻¹. Therefore, as in conventional dye lasers, a quasicontinuum exists for each electronic level comprised of the thermally broadened rotational and vibrational levels.

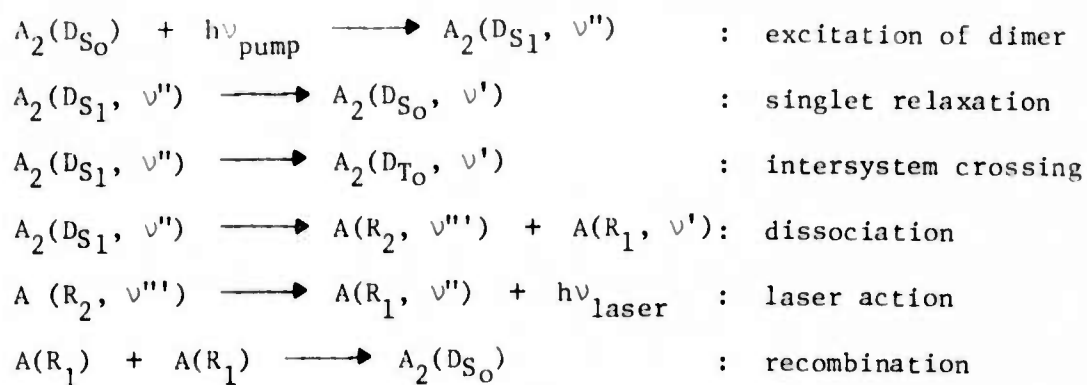
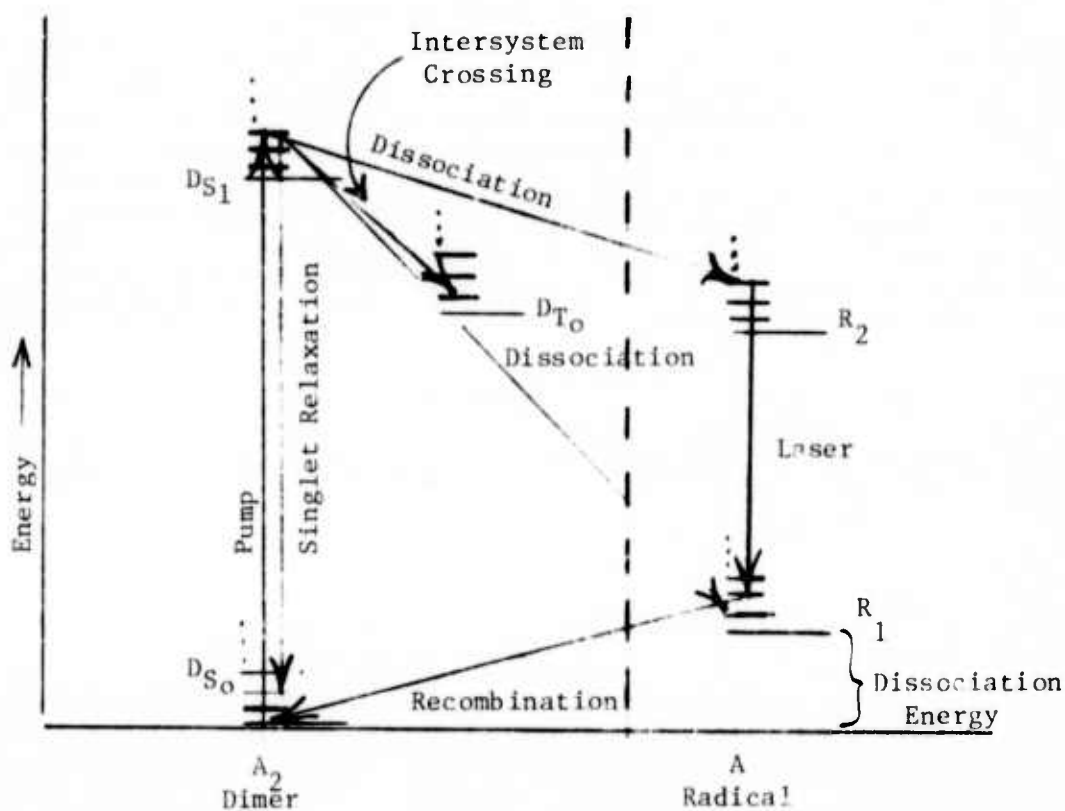


Figure 1. Photodissociation Dye Laser Molecule Structure and Kinetics

A characteristic of the photodissociation dye laser molecule is that the DS_1 and D_{T0} levels in the dimer lie above the dimer dissociation energy. Consequently, upon optically pumping the dimer to DS_1 the molecule will undergo dissociation into two radicals. Dissociation may occur via two possible paths. The first is directly from the optically pumped DS_1 level. However, the DS_1 level may, in principle, undergo a rapid intersystem crossing to the D_{T0} level. Dissociation of the dimer may occur from this level.

Upon dissociation, the excitation energy is partitioned between a manifold of levels in the quasi-continuum of both the excited and ground state of the radical. The radical ground state initially has a negligible population; consequently, a partial inversion in the radical can be produced. The stimulated emission is tunable as in conventional dye lasers due to the quasi-continuous distribution of the upper and ground levels. An interesting point is that for radicals considered suitable for the photodissociation dye laser both the calculated and measured oscillator strengths for the first doublet-doublet electronic transition are always small. Thus, even though these transitions are allowed by the selection rules, they exhibit a partial "forbiddenness". Consequently, the radiative lifetime of the laser transitions can be expected to typically be a factor of a hundred times longer than in conventional dye lasers. This has been experimentally verified as will be discussed later. The longer lived upper laser levels can permit a larger population density to be obtained and thereby allows the possibility of high power output.

The ability of the photodissociation dye laser to operate on a cw basis requires, as usual, that the depletion rate of the lower laser level exceed the radiative transition rate from the upper to the lower laser level. The lower laser level is the radical ground state which is unstable to recombination back to the original parent dimer. Thus for a steady-state population inversion to be maintained, the radical recombination rate must be greater than the laser transition radiative rate.

B. Chemical Properties of Free Radicals

Recombination is only one of many possible reaction paths that can occur in a radical system. Because they are characterized by an unbound electron, free radicals are usually very reactive. Consequently, competing processes can occur which make their production, handling, and any subsequent experimental analysis difficult. The primary radical reactions which may prove deleterious to the PDL scheme are:

(1) Disproportionation - two molecules of the radical are reduced at the expense of a third radical which is oxidized. This reaction can be catalyzed by heat or light.

(2) Irreversible Dimerization - this reaction results in an isomer of the original hexarylethane. It may be avoided by the rigorous exclusion of acids from the reaction system.

(3) Addition reactions - rapid absorption of atmospheric or dissolved oxygen to form colorless peroxide precipitates. Rigorous exclusion of oxygen is essential to minimize this reaction path.

C. Criteria for the Selection of
Photodissociation Dye Laser Molecules

There are several requirements that a photodissociation dye laser molecule must satisfy. Firstly, the dimer ground state must be thermally stable against dissociation at room temperature. Specifically, the ratio of the ground state radicals to ground state dimers at room temperature should typically be no greater than 10^{-4} . This will insure that there will be a negligible initial population in the lower laser level and that cryogenic operation would not be required.

A simple rate-equation model (see Section III-D) of the photodissociation dye laser based upon the dissociation of the dimer from the D_{S1} level can be employed to determine the dominant rate processes. Such a model shows that the steady-state population (D_{S1}) of excited singlet dimers is related to the population density of ground state dimers (D_{S0}).

$$(D_{S1}) = \frac{k_p}{k_1 + k_2 + {}^1k_D + 2k_D} (D_{S0})$$

where

- k_p = optical pumping rate
- k_1 = $D_{S1} \longrightarrow D_{S0}$ relaxation rate
- k_2 = $D_{S1} \longrightarrow D_{Tc}$ intersystem crossing rate
- ${}^1k_D, 2k_D$ = dissociation rate into the R_1 and R_2 radical levels, respectively.

The R_2 upper laser level population density, (R_2), obtained from the dissociation of the D_{S1} level is given by:

$$(R_2) = \frac{{}^2k_D k_p}{\tau^{-1} (k_1 + k_2 + {}^1k_D + 2k_D)} (D_{S0})$$

where τ^{-1} is the radiative lifetime of the upper laser level.

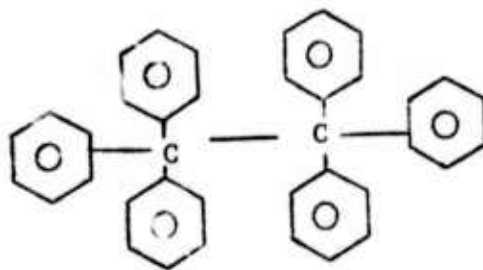
It can be seen from the above two equations that to obtain a large upper laser level population the pump rate must be large compared with the total depletion rate of the $D_{S1} \longrightarrow D_{S0}$ rates, the intersystem $D_{S1} \longrightarrow D_{Tc}$ crossing rate, and the dissociation rate to R_1 and R_2 . In addition, the dissociation rate to R_2 should be large compared to the radiative decay rate through the laser transition. The fact that in some of the candidate molecules the proposed laser transition is partially forbidden tends to well satisfy this requirement.

III. EXPERIMENTAL EFFORT AND RESULTS

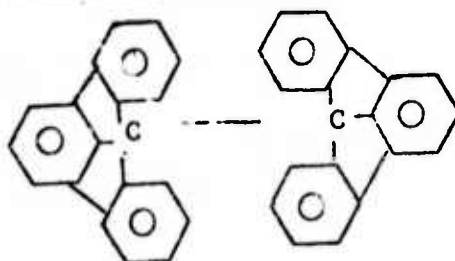
A. Photodissociation Dye Laser Candidates

A class of organic compounds known as hexaarylethanes exhibit many of the prerequisites necessary for a PDL active medium. For the purposes of this investigation five such compounds have been selected, synthesized, and purified for further study. These five are*:

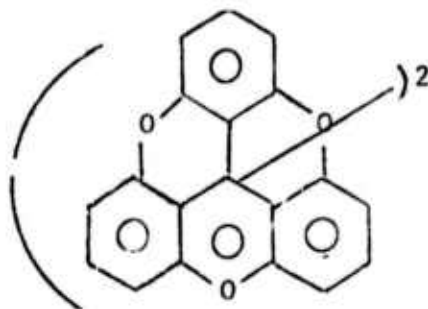
1. Hexaphenylethane



2. 12-12" Bifluoradenyl

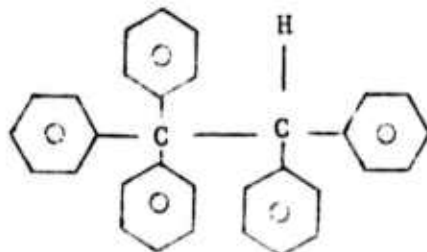


3. Sesquixanthryl

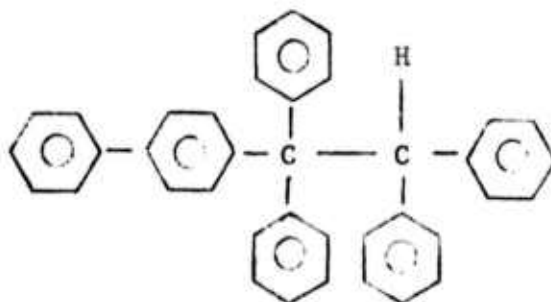


* The accepted structures of these dimer molecules are non-planar, and recent studies have shown them to possess a quinoid-type atomic arrangement. However, this does not affect in any way the proposed operation of the PDL scheme.

4. Pentaphenylethane



5. 1-p-Biphenyl-1,1,2,2-tetraphenylethane



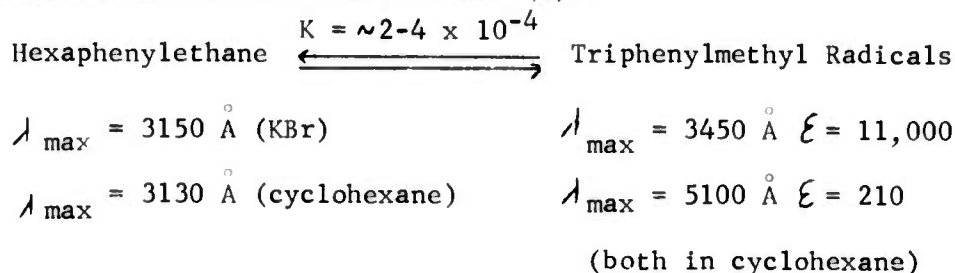
Details on the synthesis routes and experimental technique used in the preparation of these compounds are given in Appendix I. It should be pointed out that these materials are not conjugated double bond systems and therefore strictly speaking are not considered dyes according to the usual chemical usage of the word.

A summary of the relevant properties of each of the synthesized PDL molecules, based on a literature survey as well as our own observations, follows:

1. Hexaphenylethane

Historically, hexaphenylethane is by far the most well characterized of the five synthesized compounds. It is solid at room temperature, and is readily dissolved in most organic solvents to form a yellow colored solution. The color is attributed to the formation of the triphenylmethyl radical, the existence of which has been proved by a multiplicity of analytical techniques, including electron spin resonance spectroscopy. The equilibrium constant K of the dimer \longrightarrow radical reaction is $\sim 2-4 \times 10^{-4}$ at room temperature (1). Although the equilibrium condition is displaced towards the hexaphenylethane, an appreciable number of triphenylmethyl radicals are produced via thermal dissociation of the dimer. For example, using the above value for the equilibrium constant one calculates that in a 10^{-3} M solution of hexaphenylethane at room temperature, $\sim 25\%$ of the dimer is dissociated to form radicals.

The reported major bands in the electronic absorption spectra for hexaphenylethane and the triphenylmethyl radical are shown below, along with the measured extinction coefficients (2).



The major absorption bands can be associated with electronic transitions. The resulting dimer-radical energy level structure is shown in Figure 2. The first excited singlet level of the dimer D_{S1} , is $31,750 \text{ cm}^{-1}$ from the dimer ground state. The activation energy for dissociation is $\sim 7000 \text{ cm}^{-1}$ (3) while the dissociation energy is $\sim 4,000 \text{ cm}^{-1}$ (1). The ground vibrational level of the first excited electronic level in the triphenylmethyl radical lies at $19,410 \text{ cm}^{-1}$ and the second level is at $\sim 29,000 \text{ cm}^{-1}$ above the ground state.

The mirror image symmetry of the absorption and fluorescence bands for the radical is illustrated in Figure 3. The spectra shown were originally reported by Lewis et al. (4) and were measured at -190°C . The sharp features of the spectra are present even at room temperature, as illustrated in the triphenylmethyl radical absorption spectrum shown in Figure 4. This spectrum was taken in our laboratory with a Beckmann spectrophotometer. The radical is thermally produced in a solution of hexaphenylethane. The three main peaks in the absorption spectrum are quite well resolved even though the less prominent features evident in the low temperature spectra are not present.

The fluorescence lifetime of the triphenylmethyl radical has also recently been measured at low temperature (5). The radicals were prepared by the photolysis of triphenylmethane at 77°K in a quartz cell using a low pressure mercury lamp. An N_2 laser emitting a 10 nsec, 40 kW peak power pulse at 3371 \AA was used as the exciting source for fluorescence. The reproduced data are as follows:

	Lifetime (nsec)	
	In Ethanol	In Isopentane
Triphenylmethyl Radical	280	330

The very long fluorescence lifetimes were interpreted to show that the first doublet-doublet electronic transitions in this radical actually has a somewhat forbidden character, although the transitions are allowed by selection rule considerations. The possibility that the observed lifetimes are longer than the natural lifetimes because of complex formation between the excited state and the solvent can be excluded since the difference between lifetimes measured in polar and non-polar solvents was not appreciable.

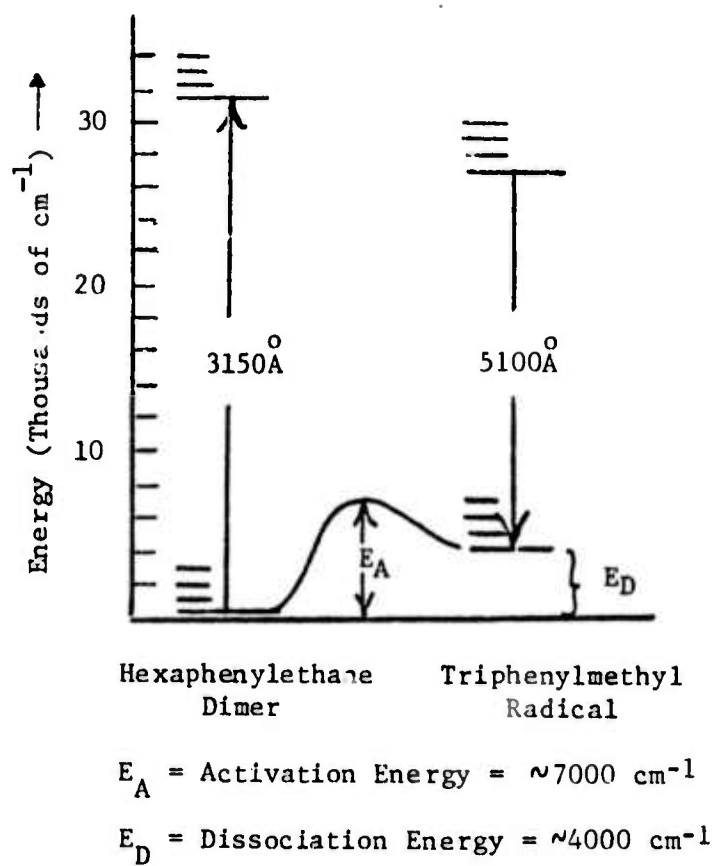


Figure 2. Energy Level Structure of the Hexaphenylethane-Triphenylmethyl System.

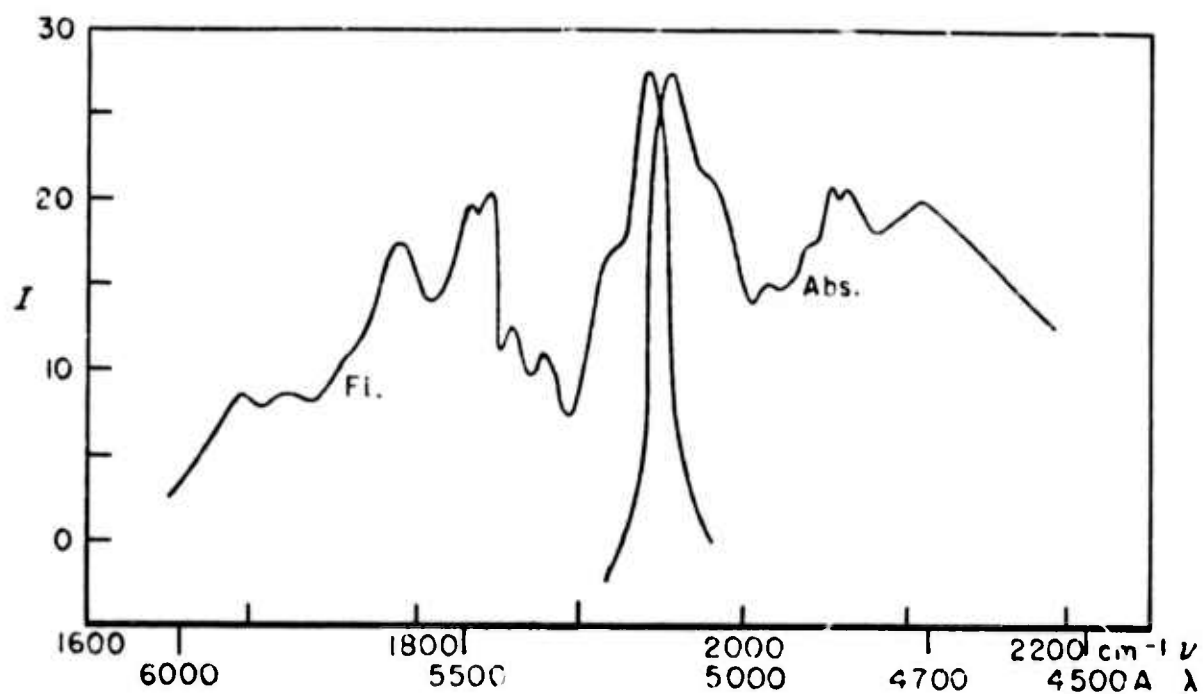


Figure 3. Mirror Symmetry of Absorption and Fluorescence Bands of the Triphenylmethyl Radical (in EPA mixed solvent at -190°C). Ref (4).

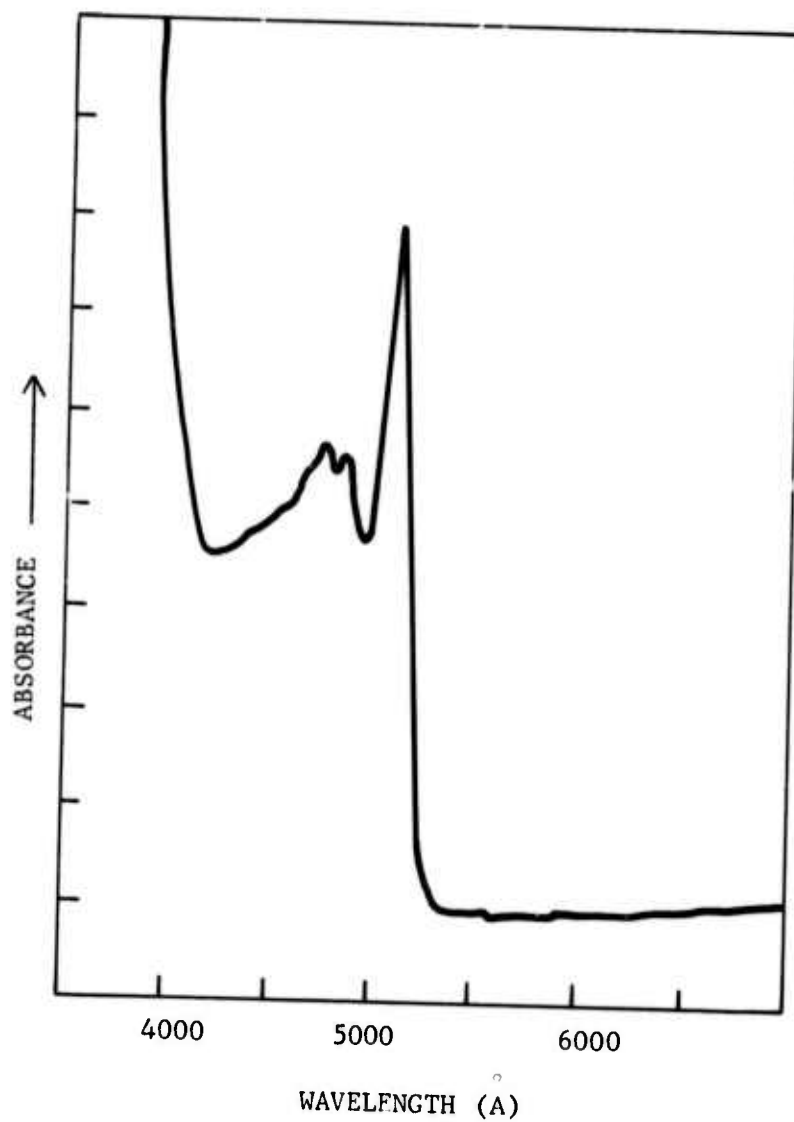


Figure 4. Absorption Spectrum of the Triphenylmethyl Radical Taken at Room Temperature. (Hexaphenylethane in Isooctane)

2. 12-12' Bifluoradenyl

This material is completely stable at room temperature, i.e. essentially no radicals are thermally produced. The UV absorption spectrum we have measured is shown in Figure 5A. The dimer absorption feature is the broad plateau region centered at $\sim 2800 \text{ \AA}$. We have calculated the extinction coefficient ϵ to be 40,000 at 2800 \AA .

Evidence has been sought in the literature for the possible dissociation of 12-12' bifluoradenyl into fluoradenyl radicals. However, published attempts, including ESR measurements, have yielded negative results.

We have looked for a color change indicative of the existence of thermally produced radicals upon heating a solution to 150°C . Again the results were negative. However, this does not exclude the possibility of radical production during photodissociation.

3. Sesquixanthryl

This material is completely stable as dimer at room temperature. At elevated temperatures ($\sim 100^\circ\text{C}$) thermal production of radicals has been observed both by noting a color change when a solution is heated as well as by ESR techniques. However, solubility studies we have performed indicate that sesquixanthryl is very insoluble in every common organic solvent except methyl benzoate. Methyl benzoate, however, absorbs strongly at $\leq 3300 \text{ \AA}$ and therefore no UV data on the dimer could be obtained.

4. Pentaphenylethane

We have obtained the UV system spectrum of pentaphenylethane as shown in Figure 5B. It exhibits a peak absorption at 2670 \AA with an extinction coefficient $\epsilon = 1800$. Historically, color attributed to radical formation has been observed in an ethyl benzoate solution at $\sim 100^\circ\text{C}$ (6).

5. 1-p-Biphenyl-1,1,2,2-tetraphenylethane

The measured UV absorption spectrum is shown in Figure 5C. Peak absorption occurs at 2600 \AA with an extinction coefficient $\epsilon = 25,000$. Color change indicative of radical formation has been observed in heated solutions ($\sim 100^\circ\text{C}$) (6).

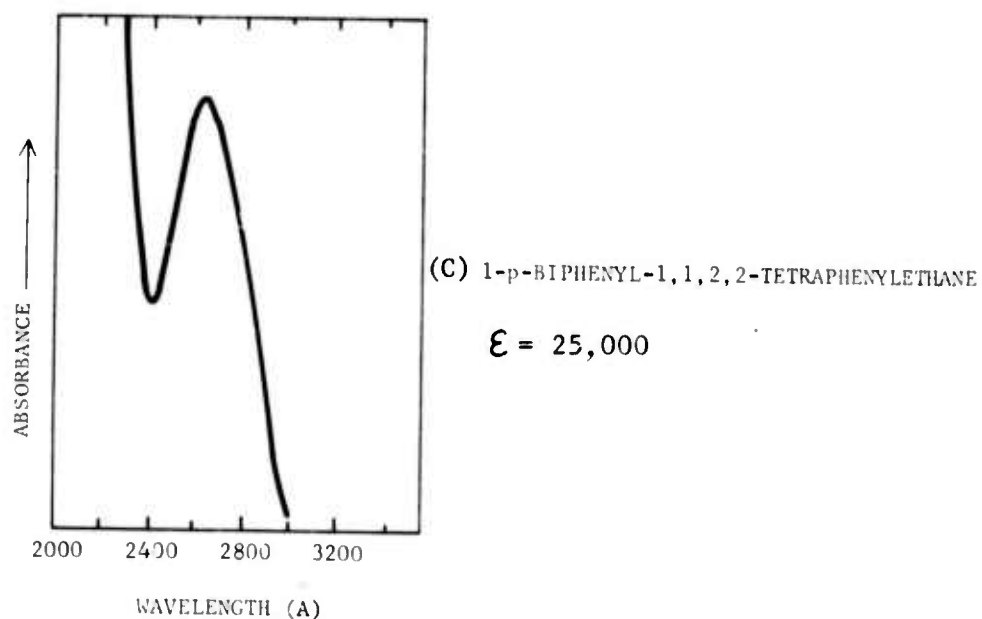
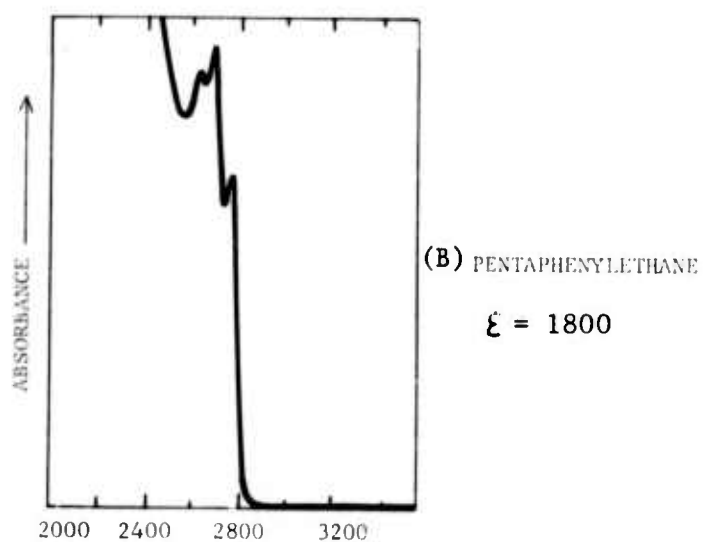
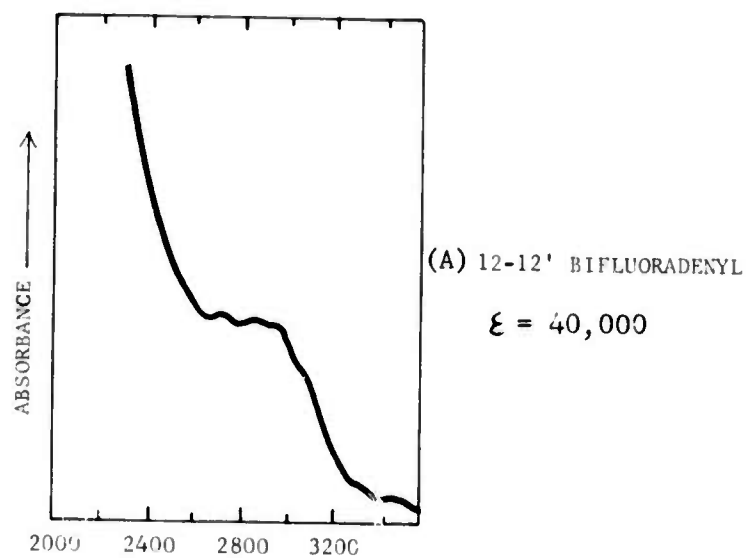


Figure 5. UV Absorption Spectra of PDL Molecules - the extinction coefficients at the peak of the dimer absorption bands are given.

B. Evaluation of PDL Materials

Sesquioxanthryl cannot be studied as a PDL system material because of its insolubility in any compatible UV solvent. Pentaphenylethane and 1-p-biphenyl-1,1.2.2-tetraphenylethane are complicated because the dissociation step leads to the formation of two distinct radicals. These radicals then enter into equilibria reactions with themselves as well as with each other. In addition, there is no data available on the absorption of fluorescence properties of the radicals that are produced. A separate experimental effort would be required to obtain such information, before meaningful measurements regarding their usefulness of PDL materials could be performed. Similarly, the lack of sufficient data on the fluoradenyl radical, even data establishing its existence, makes 12-12' bifluoradenyl a poor initial candidate.

These considerations have led us to the conclusion that hexaphenylethane is the most promising system for an initial study. Since information on the fluorescence spectra and upper state lifetime of the triphenylmethyl radical is available in the literature, a basis exists for understanding the time resolved studies that are necessary to evaluating the PDL concept. Should the results look promising, it would then be appropriate to take a closer look at the other materials we have synthesized.

It should be pointed out, however, that chemical stability problems have been encountered in working with solutions of hexaphenylethane. The thermally produced triphenylmethyl radicals undergo rapid reactions with dissolved oxygen to form peroxide precipitates (See Section IIB).

As the radicals react, more dissociation occurs in order to maintain the dimer-radical equilibrium constant. In this way, a continuous depletion of both the radical and dimer concentration occurs until all the hexaphenylethane reacts to form the peroxide precipitate.

Initial attempts at preparing solutions of hexaphenylethane involved dissolving solid hexaphenylethane in degassed solvents. The previously prepared solid hexaphenylethane was synthesized under vacuum conditions. The solvents were degassed several times under vacuum, and then added to the solute. Transfer and storage of these materials were always performed in a nitrogen atmosphere, and the final solutions were kept in o-ring sealed cells.

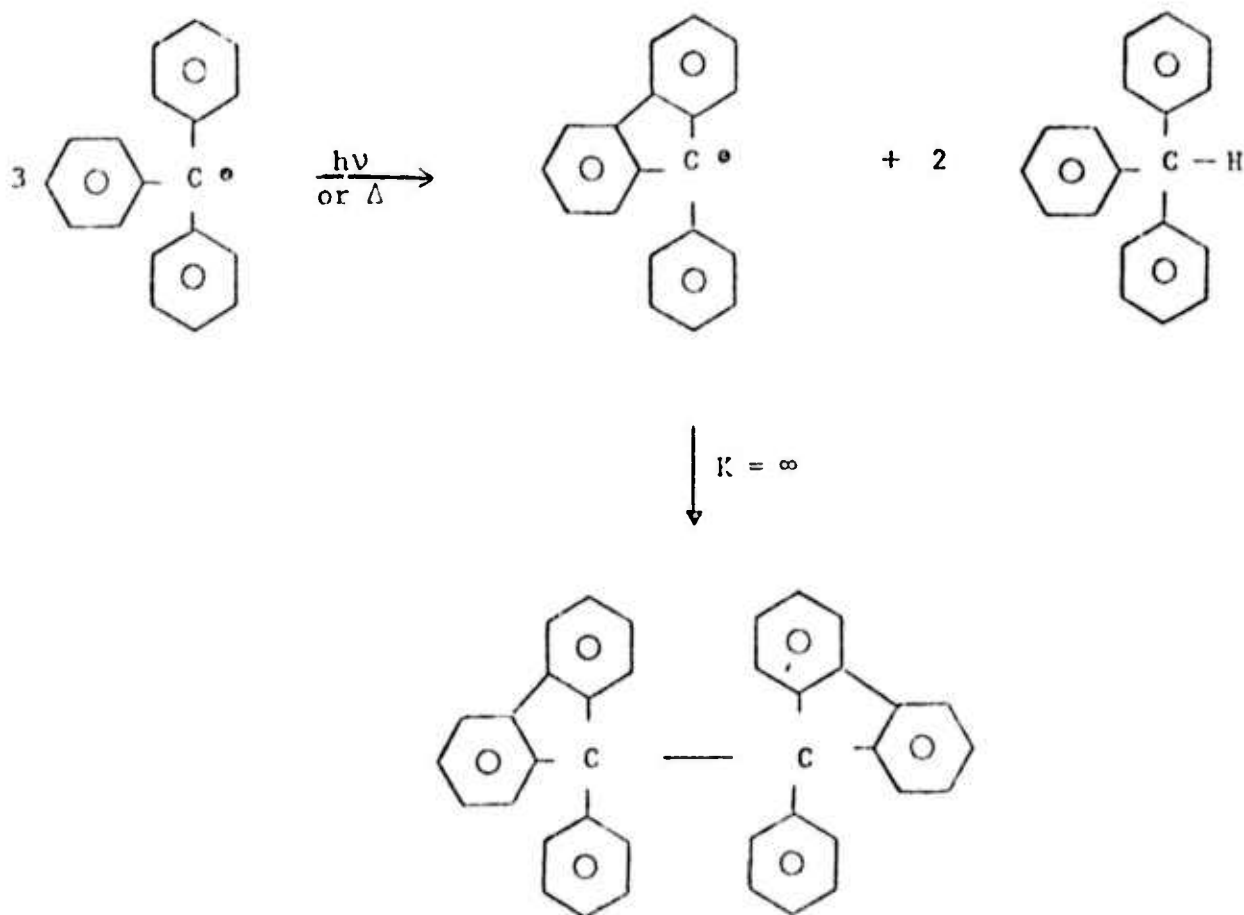
Solutions prepared in this manner were stable for periods ranging from several hours to one day. After such time, the characteristic color of the solution had visually disappeared, and precipitates had formed on the walls and bottom of the sealed cell.

Increased stability has been achieved by means of an "in situ" preparation. This technique is outlined in the appendix. Essentially, all the starting materials, required in the hexaphenylethane preparation, including solvent, are put in a sealed flask. The reaction proceeds, and the triphenylmethyl radicals that are produced are allowed to react with the dissolved oxygen until all the oxygen is depleted. The resulting hexaphenylethane solution is then filtered from the precipitate and stored under a nitrogen atmosphere.

Solutions prepared in this manner seem to be stable for much longer periods. The radical concentration can be monitored in time by measuring its absorbance with a spectrophotometer. Such measurements indicate that the decrease in radical concentration is only several percent per week. Over the time scale of an experiment (several hours) such solutions remain relatively stable. With refinement of the techniques used in preparation and handling we expect the residual oxygen content to be decreased even further.

A potentially more serious problem from the point of view of the PDL concept is photochemical stability. As mentioned in section IIB, disproportionation reactions are catalyzed by heat or light. If a solution of hexaphenylethane is placed in sunlight, the color indicative of radical formation disappears within several hours. The products formed are known to be triphenylmethane and the dehydro-dimer of 9-phenylfluorene.

The reaction is:



In essence, two molecules of the radical become reduced at the expense of a third radical which is oxidized. The rate of this reaction is clearly a strong function of concentration. The extent to which such reactions occur during the time scale of our measurements may seriously hamper our ability to understand the system from the PDL viewpoint.

C. The Laser Pump Source

The dimer absorption bands of all the PDL molecules we have synthesized are in the UV region covering a range of 2600-3200 Å. In order to study such systems a tunable UV laser source has been assembled.

The 3371 Å output of an N₂ laser is used to pump a Moletron DL 300 Dye Laser. Frequency doubling the dye output by means of KDP crystals provides a UV probe with a tunable output range of 2600-3700 Å.

Measured operating characteristics of the system are:

	<u>Energy/Pulse</u>	<u>Time Duration</u>	
N ₂ Laser	5 mj	8-10 ns	System
Dye Laser	0.5-0.7 mj	5 ns	Rep. Rate: 1-10 pps
Doubled Output	10-40 μj	5 ns	

The nitrogen laser we have built is based on a design by Woodward, Ehlers, & Lineberger (7). Basically, energy is stored in two 0.1 μf Tobe Deutchman disc capacitors connected in series. This energy is then transferred by an EGG HY 3202 thyatron switch to a low inductance transmission line consisting of 100 Belden YK-217 17Ω cables connected in parallel across the discharge electrode. A cross-sectional view of the laser assembly is shown in Figure 6.

The length of the active discharge region is 150 cm. To insure a uniform discharge along this length an N₂ flow transverse to both the discharge direction and optic axis has been incorporated in the design. Nitrogen gas enters thru evenly spaced holes positioned along the length of the ground electrode, and is pumped out through similarly positioned holes as shown in Figure 6.

An attempt to achieve travelling wave excitation was designed into the device. The lengths of the cables were staggered so that the voltage pulse at a particular point would arrive simultaneously with the light wave travelling down the tube. However, this has not led to travelling wave output. The statistical time jitter associated with the actual breakdown in the discharge after overvolting is probably greater than the 5 ns transit time of the light down the tube length, thereby averaging out any travelling wave effect.

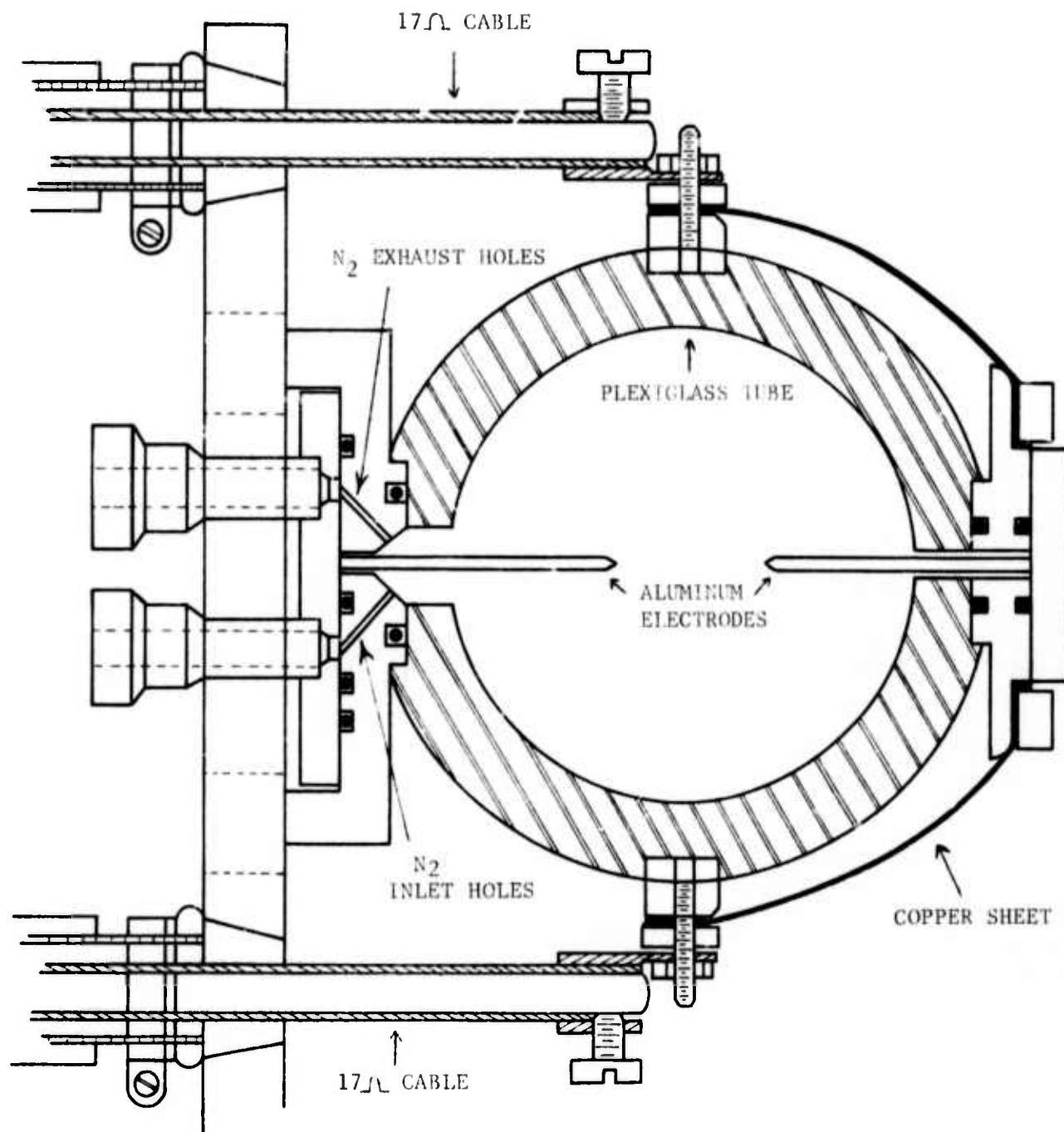
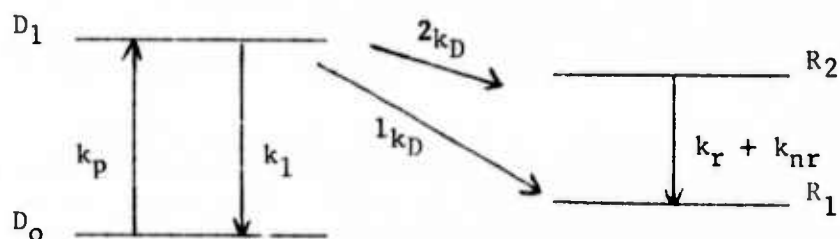


Figure 6. Cross-sectional view of N₂ laser assembly.

The present output power of the device is ~ 0.5 Megawatts at a repetition rate of 1-10 pps. We are still in the process of correcting a number of electrical breakdown problems that have been encountered in the high-voltage structure. When these problems are solved, we expect the output power to exceed 1 Megawatt.

D. Rate Equation Analysis

In order to evaluate what information time-resolved measurements of absorption and fluorescence can yield about the rates involved in the PDL scheme, the appropriate rate equations have been solved. Such an analysis has been performed assuming the following model:



The first excited dimer is pumped with a rate constant k_p . The total decay rate out of D_1 by all processes except dissociation is described by k_1 , and the dissociation rates into the upper radical state R_2 and the ground radical state R_1 are characterized by $2k_D$ and $1k_D$ respectively. The processes contributing to k_1 include fluorescence, internal conversion and intersystem crossing. In the model for which the rate equations are written the molecules in D_1 which undergo intersystem crossing return to D_0 . The radical decay is characterized by the sum of a radiative term k_r and a non-radiative term, k_{nr} . Radical recombination is neglected here so that the resulting rate equations remain linear.

Four equations may be written:

$$\frac{dD_0}{dt} = -k_p D_0 + k_1 D_1$$

$$\frac{dD_1}{dt} = k_p D_0 - (k_1 + k_D) D_1 \text{ where } k_D = 1k_D + 2k_D$$

$$\frac{dR_2}{dt} = 2k_D D_1 - (k_r + k_{nr}) R_2$$

$$\frac{dR_1}{dt} = 1k_D D_1 + (k_r + k_{nr}) R_2$$

where, D_0 , D_1 , R_2 , and R_1 , denote the time varying population densities of the respective states.

The equations have been solved assuming $k_p = \text{constant}$ for $0 \leq t \leq t_p$ and $k_p = 0$ for $t > t_p$, with the boundary conditions $D_0(0) = \text{constant}$, $D_1(0) = 0$, $R_2(0) = 0$, and $R_1(0) = 0$. This yields the time behavior after pumping with a rectangular pulse, of a system which initially consists of all ground state dimers. Several important conclusions can be drawn from the results. After the pump pulse has terminated, solution of the equations shows that the time rate of change of the upper radical level has the form:

$$R_2(t) = A e^{-(k_r + k_{nr})(t-t_p)} + B e^{-(k_l + k_D)(t-t_p)} \quad t > t_p$$

Since the intensity of fluorescence decay is proportional to the population density of the decaying state, the fluorescence decay rate of the upper radical state after the dimer absorption band has been pumped should exhibit the above time dependence. If the PDL system behaves according to our model, analysis of this decay will yield the values $(k_r + k_{nr})$ and $(k_l + k_D)$.

Fluorescence decay of the upper radical state may also be monitored after pumping the radical absorption band. In this case, since there is no dimer contribution, the observed decay rate will yield the value $(k_r + k_{nr})$. Note that both of the above experiments must be performed in order to obtain and identify the $(k_l + k_D)$ rate and the $(k_r + k_{nr})$ rate.

E. Fluorescence Measurements and Future Work

We have begun our studies by focusing attention on the hexaphenyl-ethane-triphenylmethyl dimer-radical system. This system is complicated to some extent by the fact that equilibrium condition in solution at room temperature is not pushed completely towards the dimer, as in the order PDL systems. Rather, appreciable thermal dissociation into triphenylmethyl radical does occur.

When a solution of hexaphenylethane in iso-octane at room temperature is irradiated with the 3371 Å output of the nitrogen laser, a greenish-yellow fluorescence can be observed visually. Its spectrum corresponds to the low temperature spectrum reported in the literature for the triphenylmethyl radical (see Figure 3). The multiple peaks exhibited in the low temperature spectrum, however, are not evident at room temperature.

There are two possible routes that could account for this fluorescence. Although the dimer absorption band peaks at 3150 Å, it is probably wide enough to allow the 3371 Å light to be absorbed by its long wavelength wing. The excited radical states responsible for the observed fluorescence could then be produced by dimer photodissociation.

On the other hand, as stated earlier, the triphenylmethyl radical has a strong absorption band that peaks at 3450 \AA and which corresponds to the second excited state of the radical. Since ground state radicals are present due to thermal dissociation, the N_2 laser output could be pumping these radicals to their second excited state. As in conventional dyes, rapid internal conversion to the first excited state would then occur, with subsequent fluorescence to the ground state.

In order to determine to what extent each of these channels contributes towards the observed fluorescence, a temperature dependence study of the fluorescence intensity will be performed. At a temperature low enough to insure no appreciable thermal dissociation, radical fluorescence can only be due to the dimer photodissociating into excited radical states. Demonstration of this fact is essential to the PDL scheme, and a special quartz fluorescence cell is being constructed which will allow such a low temperature study.

In addition to the above observations, the first absorption band of the thermally produced triphenylmethyl radicals has been pumped directly by a 5 ns dye laser pulse at 5150 \AA . This wavelength corresponds to the peak of the radical absorption band. The characteristic triphenylmethyl fluorescence is observed. An RCA #C 31025C photomultiplier tube and Tektronix 485 oscilloscope have been used to monitor the time dependence of the fluorescence signal as seen through a Perkin Elmer monochromator. At all points on the observed spectrum (5150 \AA - 6000 \AA), the measured lifetime is $\lesssim 5\text{-}10 \text{ ns}$. According to the rate equation analysis, this lifetime is equal to $1/(k_r + k_{nr})$. As previously mentioned, the reported lifetime (5) of the triphenylmethyl fluorescence measured at 77°K is $\sim 200 \text{ ns}$. This difference can be understood if the non-radiative rate k_{nr} is dominated by temperature dependent processes. At low temperatures, such contributions would be reduced, so that the long observed lifetime should be equal to the radiative lifetime, $1/k_r$. In order to achieve maximum possible inversion as a laser media, the PDL system should operate in a temperature regime where the radiative lifetime is the dominant decay time. Using the low temperature fluorescence cell, we will determine what this temperature has to be by monitoring the fluorescence lifetime as the system temperature is reduced.

Efforts are also underway at present to do an absolute fluorescence intensity measurement. The observed fluorescence intensity, aside from geometrical factors, is proportional to the product of the upper state density and the Einstein A coefficient. This same product determines what the maximum possible gain of a laser system can be (assuming no population in the lower state). Such a measurement will enable us to plan for experimental conditions needed to achieve laser action in the hexaphenylethane system.

IV. CONCLUSIONS

During the first six months of the PDL program, a number of accomplishments have been achieved:

A. Five promising molecules have been synthesized and their absorption spectra characterized.

B. A pulsed tunable UV source has been assembled to investigate their fluorescence characteristics.

C. Hexaphenylethane has been identified as the most promising PDL candidate for an initial study.

D. Triphenylmethyl radical fluorescence has been observed in the hexaphenylethane system. The fluorescence lifetime has been measured and a number of experiments have been outlined that will measure parameters important to achieving laser action.

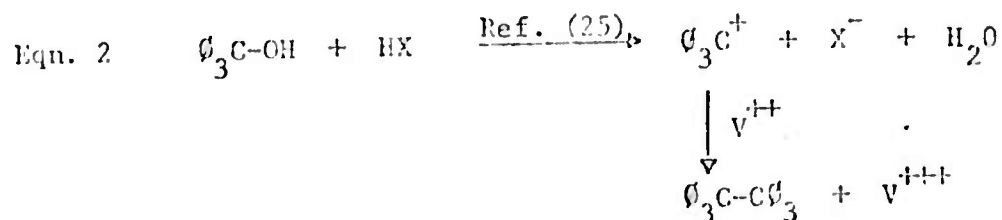
APPENDIX 1

PREPARATION OF PDL CANDIDATES

Below, we have included a summary of the established synthetic methods which are commonly employed to prepare both hexaarylethanes and tetraarylethanes. In section A, we have described the general procedures which can be used to prepare hexaarylethanes. In section B, we have outlined the reported synthetic methods which we have used to prepare the five PDL candidates described in the text.

A. General Synthetic Methods Used to Prepare Hexaarylethanes

Two standard procedures may be used to prepare hexaarylethanes. These are illustrated below in equations 1 and 2.

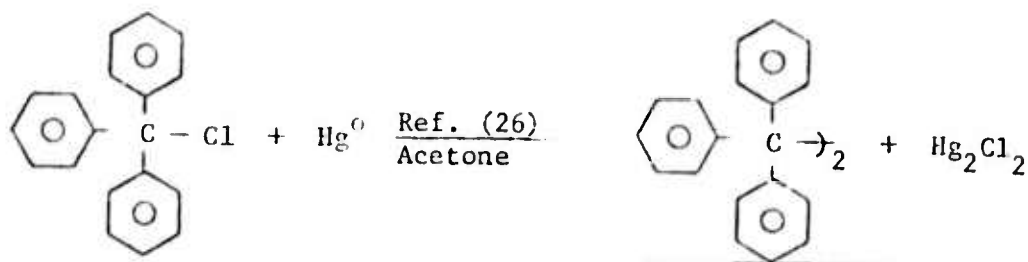


Gomberg's classical procedure (Eqn. 1) is still the method of choice. However, the second method can be generally applied for the preparation of the more sterically hindered hexaarylethanes. In both cases it is imperative that the reactions and work-ups be carried out in the absence of light and air to avoid the destruction of the free radicals formed.

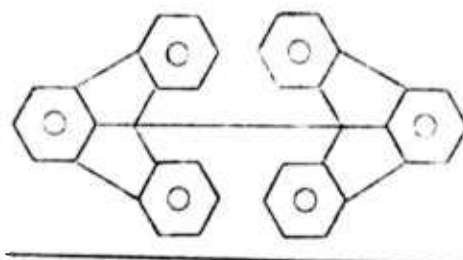
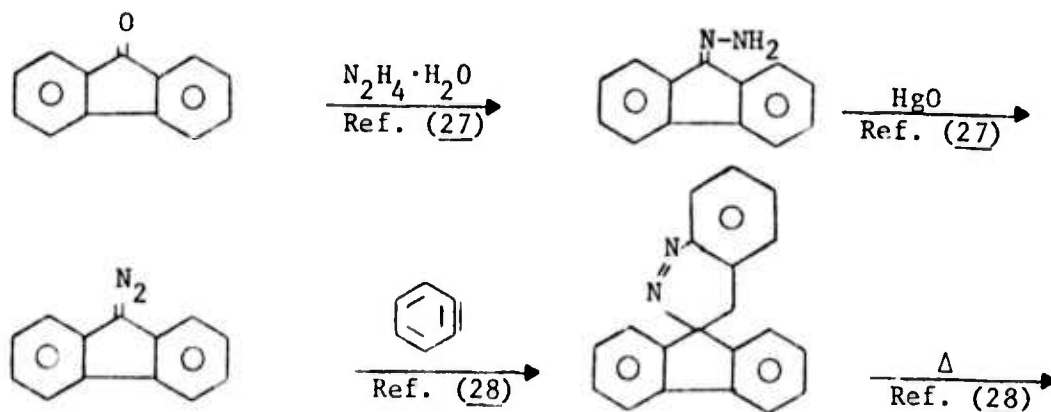
B. Preparation of Specific PDL Candidates

In the following pages, we have diagrammed, and outlined the reported synthesis routes from commercially available starting materials which we have used to prepare the prime PDL candidates.

Hexaphenylethane (A)

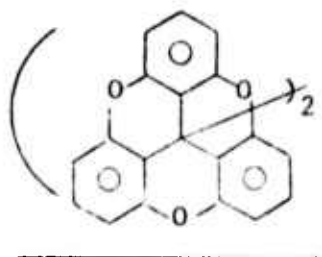
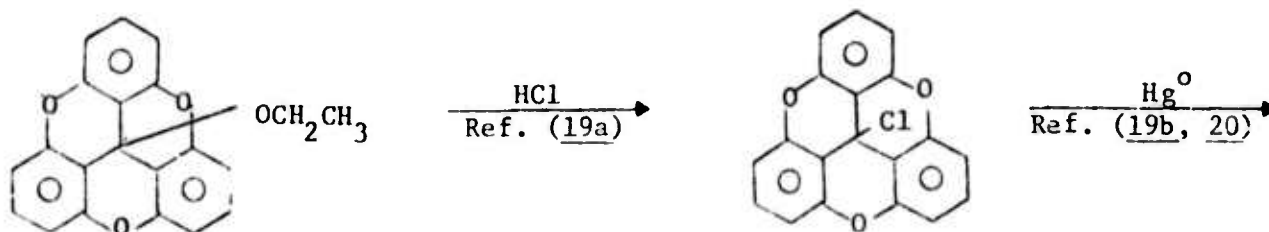
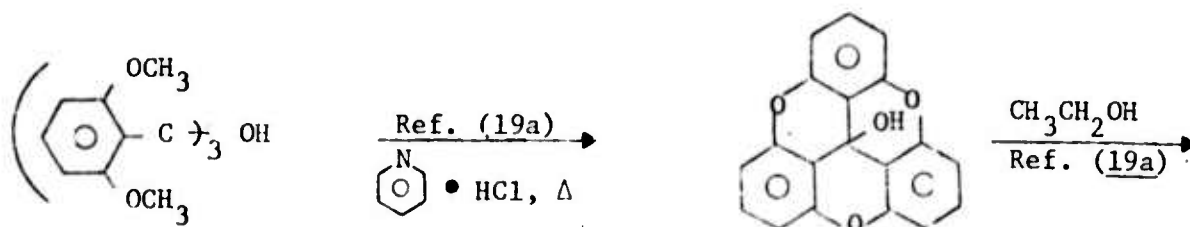
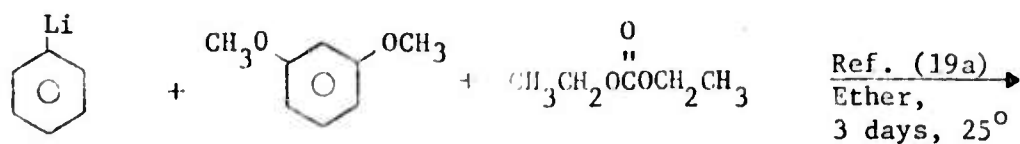


12,12'-Bifluoradene (B)

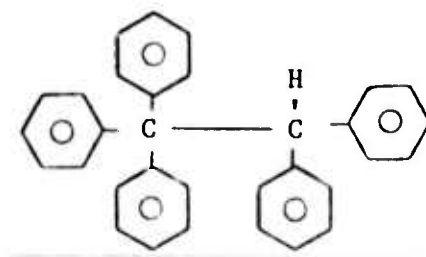
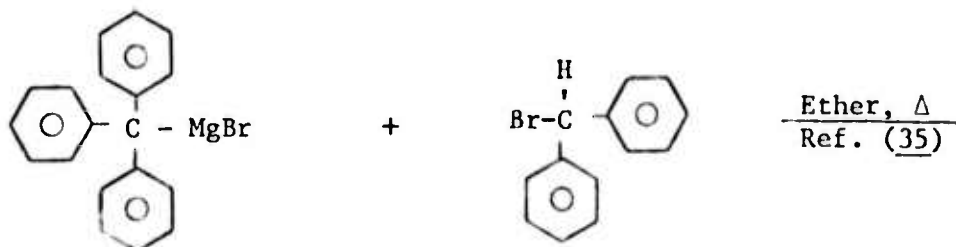


(2-40%, variable yields)

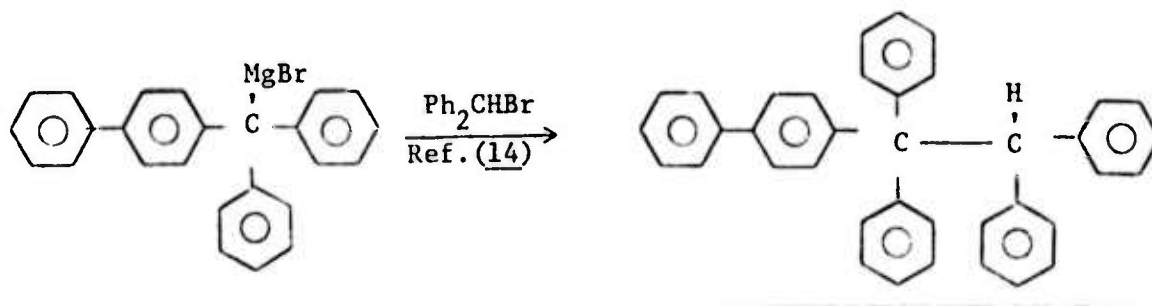
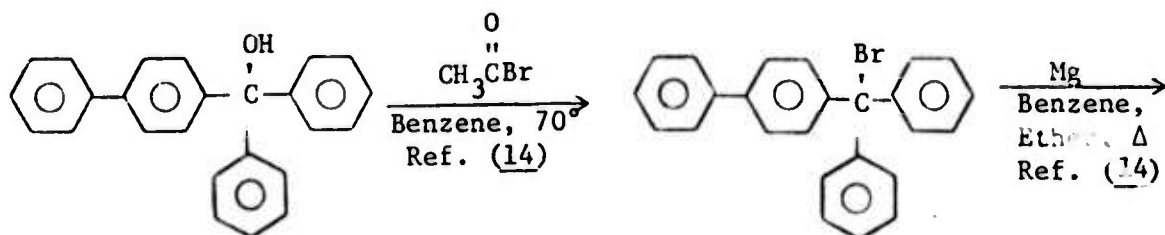
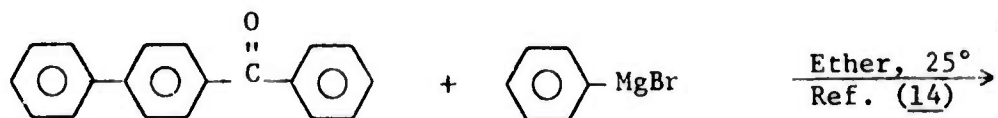
Sesquixanthdryl Dimer (C)



Pentaphenylethane (D)



1-p-Biphenyl-1,1,2,2-tetraphenylethane (E)



• Hexaphenylethane (In Situ Preparation)

The starting materials for the in situ preparation of hexaphenylethane were purified in the following manner. Triphenylmethyl chloride was purchased from the Aldrich Chemical Company and was obtained as a colorless crystalline solid after sublimation at 110-115° (0.01 mm). It was stored in a nitrogen-dry box and exposure to the air was kept to the absolute minimum. Spectro-quality 2,2,4-trimethylpentane was purchased from Ace Scientific Supply Company, Inc. and was used as received. Triply distilled, electronic grade mercury was purchased from Alfa-Ventron and was also used as received. All glassware used for the in situ preparation of hexaphenylethane was washed well with acetone, distilled water, dilute hydrochloric acid, dilute ammonium hydroxide, and then finally repetitively washed with distilled water. The excess water was drained from all the glassware, and the reaction flasks, filtering apparatus, etc. were connected to a vacuum rack and evacuated to ca., 10^{-3} mm. by means of an oil diffusion pump. The residual traces of water were then removed by evacuating the glassware for several hours with the intermittent application of external heat via a heat gun.

An "O" ring-sealed, vacuum flask was then charged with the purified triphenylmethyl chloride (0.400 g, 1.435×10^{-3} mole) and about 210 ml of the spectroscopically pure 2,2,4-trimethylpentane. This reaction flask was then sealed by firmly clamping to an "O" ring head which was equipped with two exit vacuum stopcocks. The reaction flask was then attached to the vacuum rack and about 5 ml. of the solvent was removed under reduced pressure. In this manner, most of the dissolved oxygen was removed without recourse to the conventional freeze-pump-thaw cycles. The reaction flask was then transferred to a nitrogen-dry box, and the mercury (10.0 g, 49.8 mmole, 34.7 mole eq.) was added all at once. After sealing the flask, it was completely wrapped with aluminum foil. All ensuing operations were conducted in the complete absence of light or exposure to air. The flask was then reattached to the vacuum system, and the solvent removed under high vacuum to a predetermined 200 ml. mark on the reaction flask. The flask was then sealed under the partial vacuum and was clamped in a horizontal position in a Burrel Model BB, "wrist action" shaker. After shaking for a total of fifteen hours at a constant speed setting of 10, the flask was allowed to stand overnight to allow the inorganic by-product and excess mercury to settle. The clear yellow-orange supernatant was then filtered through a "fine" glass frit into a previously cleaned and evacuated reaction flask. This solution of hexaphenylethane in 2,2,4-trimethylpentane exhibited an absorbance of 0.47 at 5150 Å. It has been stored for a period of 1-2 months in a nitrogen-dry box with no visual loss of color or precipitation of the peroxide. Also, its ultraviolet spectrum was identical to that observed for crystalline hexaphenylethane (8) which was redissolved in degassed solvent.

• 12,12'-Bifluoradene

As reported in the literature (9), a concentrated solution of spiro-(fluorene-9,3'-indazole) (10.0 g, 37.3 mmole, 10), in 80 ml. of decalin was slowly heated to reflux (186°) employing a magnetic stirrer and nitrogen bubbler-cap. The dark solution effervesced fairly vigorously near 170°. This initial reaction subsided after thirty minutes at reflux, and the dark solution was kept at a reflux for a total of one hour. The dark solution was then cooled to room temperature and stirred overnight. The resultant light tan suspension which formed was filtered to afford 12,12'-bifluoradene as a yellow-tan solid in 25% yield (2.2 g, m. pt., 304-306°). This material was obtained in analytically pure form after drying at 50° (0.10 mm) for one day:

Analysis:

Calc. for $C_{38}H_{22}$: C, 95.37; H, 4.63

Found: C, 95.23; H, 4.92

• Sesquixanthryl Dimer

By analogy to the reported procedure (11), reformed sesquixanthryl chloride dihydrate (2.0 g, 5.6 mmole, 12) was dissolved in a mixture of 150 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid. A dilute solution of the commercially available chromous chloride (Fisher Scientific Company) was then added dropwise with efficient stirring under a nitrogen atmosphere. A yellow suspension formed immediately upon the beginning of the addition of the chromous chloride solution. The addition was stopped after the reaction mixture assumed a permanent blue color (ca., 120 ml. of $CrCl_2$ solution), and 200 ml. of water was added dropwise. Filtration afforded the crude dimer as a yellowish tan solid in an overall yield of 1.3 g. The analytical pure dimer was obtained after drying at 100° (0.10 mm) for 24 hours (m. pt. 300°).

Analysis:

Calc. for $C_{38}H_{18}O_6$: C, 79.99; H, 3.18

Found: C, 79.18; H, 3.62

• Pentaphenylethane

As previously described in the literature (13), a solution of triphenylbromomethane (32.3 g, 0.10 mole) in 100 ml. of benzene was added dropwise into a suspension of magnesium turnings (2.5 g) in 50 ml. of ether under a nitrogen atmosphere at room temperature. The mixture was then refluxed overnight to complete the formation of the Grignard reagent. The mixture was then cooled to room temperature and the solution was decanted from the unreacted magnesium into a fresh four-neck flask. Solid diphenylbromomethane (27.8 g, 0.10 mole) was then added portion-wise with efficient stirring and cooling with an external water bath. The mixture was then heated for two hours on a steam bath and allowed to stir overnight at room temperature. A 3% solution of acetic acid in water (50 ml.) was then added dropwise with efficient stirring. The organic layer was then separated and the solvent removed under a nitrogen purge. The white solid thus obtained was recrystallized twice from chloroform-ethanol. The analytically pure pentaphenylethane was obtained as a white solid in an overall yield of 12.0 g after drying at 25° (0.10 mm).

Analysis:

Calc. for $C_{32}H_{26}$: C, 93.62; H, 6.38

Found: C, 93.08; H, 6.51

• 1-p-Biphenyl-1,1,2,2-Tetraphenylethane

As reported by Bachmann and Wiselogle (6), diphenyl-p-biphenyl-magnesium bromide was first prepared by heating to reflux a mixture of diphenyl-p-biphenylbromomethane (20.0 g, 1) and magnesium turnings (1.23 g) in 25 ml. of ether and 50 ml. of benzene. The mixture was protected from light by an aluminum foil wrap and was refluxed for a total of ten hours. The characteristic red color of the free radical, diphenyl-p-biphenylmethyl, developed immediately and gradually gave way to the lighter brown color of the Grignard reagent. A solution of the commercially available bromodiphenylmethane (12.35 g) in the minimum quantity of dry benzene was then added fairly rapidly into the reformed Grignard reagent. A moderate exotherm was noted during this addition. The mixture was refluxed for two hours, cooled to room temperature, and then hydrolyzed by the dropwise addition of 100 ml. of 1 M acetic acid. The organic layer was separated and the solvent removed under a nitrogen purge. The dark red oil was then recrystallized three-times for chloroform ethanol. After drying at 80° (0.10 mm) for four hours, the title product was obtained in pure form as a white solid in an overall yield of ca., 3.0 g (m. pt., 173-175°).

Analysis:

Calc. for $C_{38}H_{30}$: C, 93.79; H, 6.21

Found: C, 93.36; H, 6.83

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